

The Effect of Temperature on Liquid Product Composition from the Fast Pyrolysis of Cellulose

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Introduction

In recent years, a good deal of attention has been focused on the thermal conversion of biomass to gases and liquids, and in particular, on the products obtainable from short time, high temperature pyrolysis of wood and other lignocellulosics. This flash pyrolysis is usually carried out at or near atmospheric pressures, while hydropyrolysis commonly employs hydrogen pressures to 20 MPa.

Residence times of only a few seconds or less with reaction at high temperatures requires a reactor configuration capable of very high heating rates. Two of the most appropriate designs are the entrained flow reactor, and the fluidized bed reactor. Many flash pyrolysis studies have employed one or the other of these reactor types.

In general, two approaches to flash pyrolysis of biomass have been used by various workers. One approach has the objective of producing a maximum yield of a desirable gas, which in atmospheric pressure non-catalytic pyrolysis processes is usually ethylene, or other olefins. Examples of processes for this purpose, such as "ultrapyrolysis" (10)(17), "ablative pyrolysis" (7), the flash pyrolysis process described by Antal (2) and the fluidized bed process of Kuester (14) have been studied in recent years for the production of olefins. These processes are characterized by high temperatures $>(650^{\circ}\text{C})$ and residence times of 1 second or less.

A second approach to flash pyrolysis has been described by Scott and Piskorz (19)(20) and Scott et al. (21). In these publications the development has been outlined of an atmospheric pressure flash pyrolysis process utilizing a fluidized bed of solid as heat carrier. The process studied has as a primary objective the determination of conditions for maximum yield of liquids from biomass, particularly forest materials. Results indicated that at apparent vapor residence times of about 0.5 seconds, organic liquid yields of 60%-70% on a moisture free basis could be obtained from hardwoods such as aspen-poplar and maple. Lower but still high yields of organic liquids (40%-60%) could be obtained from agricultural wastes such as wheat straw, corn stover and bagasse.

More recently, Knight et al. (11) have described the operation of an entrained flow reactor for the production of liquids. A somewhat different upflow entrained pyrolyzer for the production of liquids from wood has been described by Beaumont (5). Kosstrin (12) has also used a fluidized bed for thermal conversion of biomass to liquid. In general, processes for the attainment of high liquid yields operate at much lower temperatures, commonly 450°-550°C than do processes to yield gaseous products, but at about the same vapor residence times of about 500 ms.

In rapid pyrolysis processes, the rate of heat transfer is all-important. Ideally, in such a process, the time required for a biomass particle to reach about 95% of the reaction temperature would be much less than the particle residence time itself. The residence times normally quoted in thermal pyrolysis studies are usually mean gas residence times, that is, the net empty reactor volume divided by the volumetric flow rate, usually taken at reactor inlet conditions. Particle residence times are not as precisely known, and will vary with the reactor configuration and type. Measurement of mean particle residence times has not been done in the majority of fast pyrolysis process studies. However, Berruti (6) measured these residence times in a fluidized sand bed for 1 mm wood particles, and found that these varied from 2 to 6 s depending on the gas residence time (400 to 800 ms). Recently, Solomon et al. (22) reported measurements of the velocity of fine coal particles in a downward flow entrained reactor and found these were only about 40% of the gas velocity over most of the reaction period. Therefore, although the residence time of particles is generally not known very precisely in fast pyrolysis processes, it will likely be from 2 to 10 times the apparent gas residence time for most of the applicable reactors, that is, for entrained flow, fluid bed, spouted bed or cyclonic reactors. It is likely, therefore, that given a reactor capable of high heat flux, and particles of appropriate size with the "normal" gas residence time of about 500 ms, the heat-up time may not be a large fraction of the total particle residence time.

It is likely that each process will have its limits such that inadequate heat transfer causes marked changes in the distribution of the pyrolysis products. However, within these limits (which may not differ very much for different reactors capable of high heat transfer rates), the product distribution at a given gas residence time might be expected to be a function of the final reaction temperature only, especially if particles are smaller than about 1 mm and are reasonably dry. The principal criterion for this to be true is that the heat-up time for the particle should be considerably less than the time spent near reaction temperature, possibly only 20% of the total particle reaction time. As a result, the kinetic rate of reaction will probably be the rate limiting process. An equivalent criterion due to Lidén (16) would be to require that a particle reach decomposition temperature e.g. 450°C before any significant weight loss is observed.

Experimental

For this work, two completely different pyrolysis reactors were used, operated by two different research groups. The "ultrapYROLYSIS" entrained flow reactor was developed by workers at the University of Western Ontario, and was capable of operation to 1000°C with gas residence times of 50 ms to 900 ms (10). The second reactor was the fluidized bed pyrolysis unit developed at the University of Waterloo for thermal conversion of biomass to liquids (20). It operated up to 750°C with gas residence times of 300 to 1500 ms. Typical operating ranges for the two reactors are summarized in Table 1. Detailed descriptions of the respective apparatus and procedures are given in the two articles cited.

Table I Range of Experimental Parameters

	UltrapYROLYSIS	Fluid Bed
Temperature, °C	700-1000	400-750
Reactor Residence Time (Gas), ms	50-900	300-1500
Maximum Feed Rate, kg/hr	1.0	3.0
Estimated Heating Rates, °C/s	10 ⁴ -10 ⁵	10 ⁴ -10 ⁵
Pressure, atm abs.	1.0	1.0
Reaction Atmosphere	N ₂	N ₂ or Product Gas

In all tests reported here, only one feed material was used, Avicel PH-102 microcrystalline cellulose. Both groups of experimenters used samples from the same lot, which at time of use had moisture content from 2.9-4.0%, with ash <0.1%, and C 44.24, H 6.16, O 49.6. Particle size range was -250 +40 µm with a mean particle diameter of 100 µm.

Results

The pyrolysis experiments in the fluid bed were all carried out at gas residence times of 450-550 ms. In this range, yields of liquid, gas and char show only a small variation with time. Pyrolysis in the transport reactor over the reaction time span of 350-900 ms, showed that the yields of liquid, char and gas became nearly independent of residence time in the reactor. Accordingly, yields from the transport reactor in this asymptotic range at 500 ms were compared to data from the fluidized bed pyrolyzer. All data were reported as percent by weight of the moisture free feed of total liquids (including water of reaction), gas and

char. Yields were normalized to 100% by correcting the liquid yield. In all experiments, material balances were generally $\pm 5\%$ or better, and the major errors were considered to reside in losses of the most volatile liquids during liquid recovery, and inaccuracies in the water balance. Also, methanol was normally used as the solvent for recovery of tars from lines and condensers, which means that methanol yields could not be determined.

The results of pyrolysis experiments with Avicel cellulose are shown in Figures 1-4 with all data presented on a dry feed basis. Figure 1 shows that over the temperature range of 450°C-900°C the yields of gas, char and liquids from two different reactors, operated by two different research groups, are in very close agreement. Figures 2 and 3 show the variation in CO and CO₂ yields with temperature over the same range. Again, agreement of the two sets of results is very good. Yields of hydrocarbon gases are shown in Figure 4, and the good agreement of data from the two reactors is again evident for both CH₄ yield and C₂H₄ + C₂H₂ yield.

Liquid products from the pyrolysis tests were obtained over a temperature range of 375°-700°C. These liquids were analyzed for specific chemical components using methods described elsewhere (18). Results for nine of the more significant components obtained in a water extract of the tars are shown in Figures 5-8. All of these results were obtained using the fluid bed pyrolysis system of the University of Waterloo. It is apparent that at a constant reaction time, well defined and fairly narrow optimal temperature ranges exist corresponding to the maximum yields for each component.

Discussion

In order to determine if the criterion of the ratio of heat-up time to time at reaction temperature is $\ll 1.0$, it is necessary to estimate heat transfer rates in the reactors and for the particles used. If the ideas of Kothari and Antal (13) are accepted, the time required for the centre of a particle to approach 500°C would represent the heat-up time. Lede (15) comes to similar conclusions for pyrolysis at high heat fluxes, but sets the decomposition temperature at 466°C for wood. The most extreme case, that is, the longest heat-up time in the present work, would be for the largest particles at the lowest reactor temperatures. The center point temperature was calculated for 600 μm and 100 μm particles for the heating conditions of a fluidized bed (16), for a reactor temperature of 500°C with feed at 20°C. The time required for the particle mid-point temperature to reach 450°C was found to be 618 ms for the 600 μm particle and 62 ms for the 100 μm particle. Inasmuch as the solid particle residence times for the larger particles were from 2 to 6 seconds in the fluidized bed, and for smaller particles in the transport reactor were at least 500 ms, the criterion of ratio of heat-up time/available reaction time $\ll 1$ is well satisfied for all the work reported here.

Another approach was taken by Lidén (16) to estimate the importance of the heat-up period. On the basis of low temperature pyrolysis results reported in the literature, and the results obtained in our laboratory, it was assumed that if the particle temperature reached at least 450°C before more than 10% of the wood decomposed (as measured by a rate-of-weight loss kinetic expression) then excessive char production would be avoided, and the condition for high tar yields would be met, since tar decomposition would be minimized by the rapid volatilization and removal of tar components. Assuming a first order weight loss expression, this heat-up time criterion can be expressed as

$$\ln \left[\frac{1}{0.9} \right] \geq \int_0^{t_c} k [T(t)] dt \quad (1)$$

where t_c is the time required for the particle centre to reach 450°C and $T(t)$ are the set of functions describing the particle centre temperature as a function of time after introduction of feed into the reactor. The value of the first order rate constant, k , used should be one which is applicable for the rate of weight loss of the biomass species used. For the purposes of evaluating the above criterion, the kinetic parameters for the rate expression describing the total decomposition of wood as given by Thurner and Mann (23) were used, that is

$$k = 2.468 (10^6) \exp - 106.5/RT \quad s^{-1} \quad (2)$$

where the activation energy is given in kJ/mole.

Numerical integration of the right hand side of equation (1) for hardwood particles in a fluidized bed reactor at 500°C shows that for all particle sizes less than 2 mm diameter the criterion will be satisfied. It follows that for all the data presented here for the two reactors, the particles were heated throughout to at least 450°C, even at the lowest reaction temperatures, before any appreciable weight loss occurred from them. Under these conditions, then, the product distribution from either reactor for the same gas residence times could be expected to be a function of reactor temperature only, even though biomass solids were well mixed in one reactor, and in plug flow in the other.

Recently, Lidén (16) and Diebold (8) using different reactor configurations have presented very similar kinetic models for the secondary decomposition of primary pyrolysis tars from biomass. The kinetic steps for which rate constants were evaluated are proposed to be parallel initial first order decompositions, one yielding volatile liquids, while the other yields char and gas, with respective rate constants k_1 and k_2 . The ratio of k_1/k_2 in both models was assumed to be a constant with respect to temperature and to represent a theoretical maximum (ultimate) liquid (or tar) yield. The volatile organics were then assumed to decompose by another first order process to lower molecular

weight products, because experimental results for short time pyrolysis suggest that little secondary char is formed in this step (see Figure 1). Experimental results also suggest that the primary decomposition step is largely completed before significant loss of tar yield occurs, as evidenced by a nearly minimum char yield at the maximum liquid yield, as well as low gas yields at this point. As tar yield decreases due to secondary decomposition reactions, gas yield increases proportionally. It becomes possible, then, to neglect the rate of the tar forming step and to express the change of tar yield due to secondary reactions by a simplified kinetic expression, given by both Lidén (16) and Diebold (8) as

$$x = \frac{x_0 [1 - \exp(-k_3 \theta)]}{k_3 \theta} \quad (3)$$

where x is the fractional tar yield, x_0 is the theoretical "ultimate" tar yield, k is the first order constant for the tar decomposition step and θ is the reaction time for the vapor phase. The values used for the reaction parameters for tar decomposition were

Lidén $k_3 = 3.1 \times 10^6 \exp(-107500/RT) \text{ s}^{-1}$ $x_0 = 0.703$

Diebold $k_3 = 1.551 \times 10^5 \exp(-87634/RT) \text{ s}^{-1}$ $x_0 = 0.78 \text{ or } 0.76$

Liden's parameters are based on experimental data from hardwood (poplar) pyrolysis in a fluidized bed, while Diebold's values are obtained from measurements of the ablative pyrolysis of softwood followed by thermal cracking of the pyrolysis vapors.

Equation (3) was applied to the results from the pyrolysis of Avicel cellulose with prediction as shown in Figure 9. In applying equation (3) to these results, the ultimate yield, x_0 , was assumed to be 100%, although the low temperature results suggest a value slightly less than this might be more appropriate. Similarly, the yield of water was neglected, although it ranges from 2%-5%. The predicted tar yields as shown in Figure 9 are in remarkably good agreement with experiment, considering the assumptions of the model, and the fact that parameters derived from wood pyrolysis are being used to predict yields from the pyrolysis of a microcrystalline cellulose. Further, no effort was made to optimize values of the parameters with the experimental data, but only to use the values of Lidén or Diebold.

In summary, equation (3) appears to give a reasonable description of the complex cracking reactions in which biomass pyrolysis tars are converted to gaseous products, at least over the temperature range of about 500°-900°C, and for short vapor phase reaction times.

The yields of individual components shown in Figures 5-8 suggest strongly that a series of sequential decomposition steps is occurring. However, it is not clear from these results what

the precursor for any particular compound may be, or what system of parallel or sequential reactions can satisfactorily explain the nature of the variation of yield with temperature. More extensive analyses of these data are now underway.

Acknowledgement

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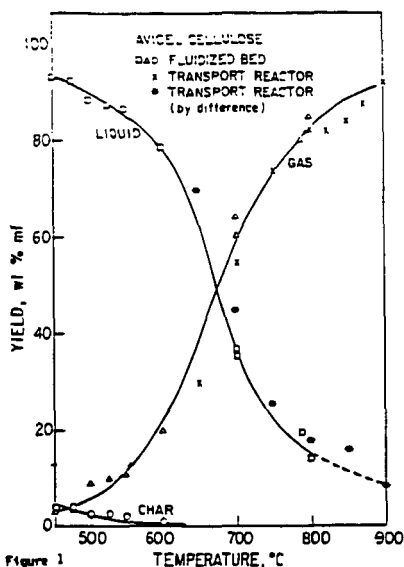


Figure 1 Product Yields from Avicel Cellulose for Two Reactors

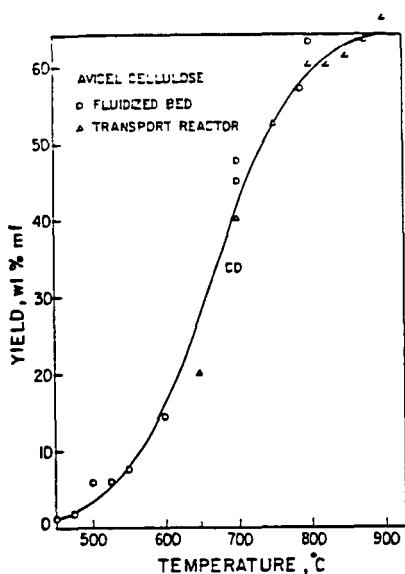


Figure 2 Yield of CO from Avicel Cellulose

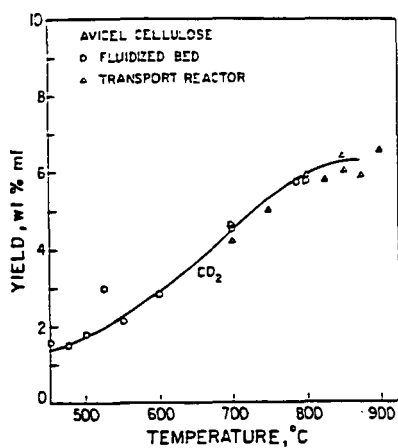


Figure 3 Yield of CO₂ from Avicel Cellulose

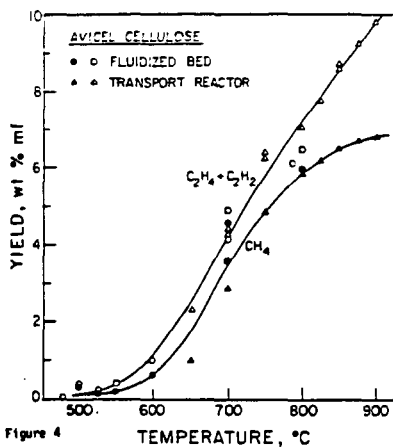


Figure 4

Yield of Hydrocarbon Gases from Avicel Cellulose

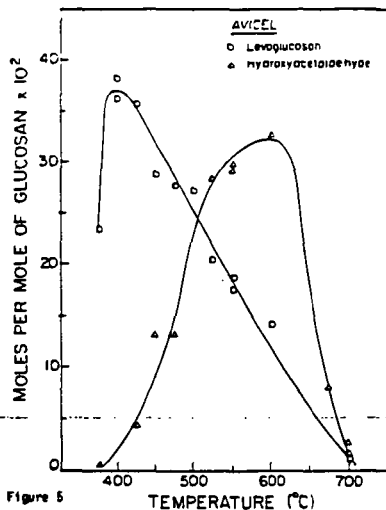


Figure 5

Yields of Levoglucosan and Hydroxyacetaldehyde, 800 ms, Fluidized Bed

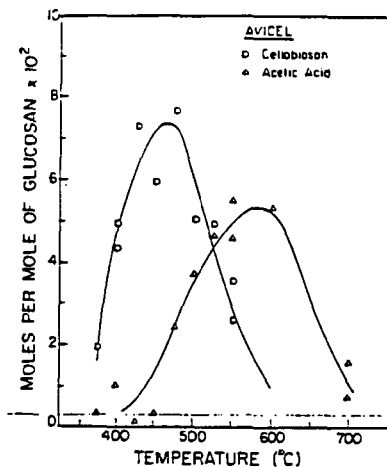


Figure 6 Yields of Cellobiosan and Acetic Acid, 500 ms, Fluidized Bed

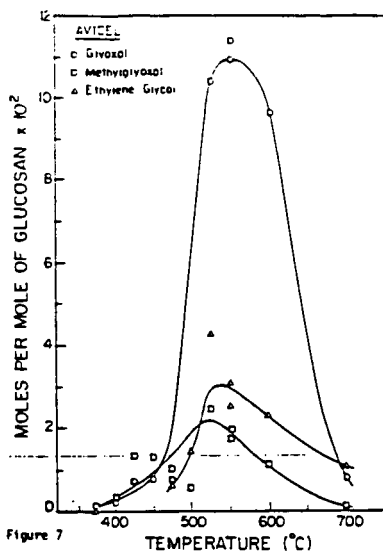


Figure 7 Yields of Glyoxal, Methylglyoxal and Ethylene Glycol, 500 ms, Fluidized Bed

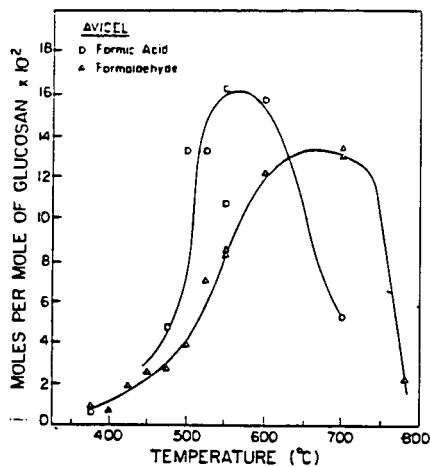


Figure 8 Yields of Formic Acid and Formaldehyde, 500 ms, Fluidized Bed

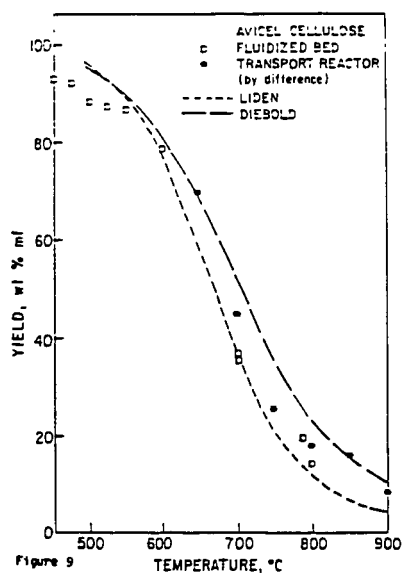


Figure 9 Prediction of Total Liquid Yields from Avicel Cellulose

PRELIMINARY ENGINEERING DATA FOR SCALE UP
OF A BIOMASS VACUUM PYROLYSIS REACTOR

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INTRODUCTION

The thermal decomposition of wood into charcoal and tar is an old process. One example of the existing technology for wood carbonization is the Lambiotte process. The ATOCHEM plant located in Premery, France, is based on the principle of external gas circulation and is a completely continuous process (1). The heating gas moves upward in the retort and constantly releases its heat into the wood, which is moving downward. The annual wood charcoal production of this plant is nowadays 20 000 t. The charcoal finds its use in the barbecue and the iron industries. Another example is the Brazilian beehive kiln for charcoal production in a batch mode. In Brazil, charcoal is mainly sold to the iron, the cement and the barbecue industries. In 1986, the total annual production of wood charcoal in Brazil was 7.5×10^6 t (2).

The recovery of by-products is important for the economy of both processes. The French recover high-value chemicals such as food aromas from the pyrolygneous liquors (3). The Brazilians market the wood tar by-product as a bunker fuel oil (4). However, further studies are still needed and are being conducted by the industry in order to make a greater and a better use of the tar and oil fraction.

Laboratory (5) and Process Development Unit (6,7) studies originally conducted at the Université de Sherbrooke, and now conducted jointly with the private industry at the Université Laval, have led to the conclusion that thermal decomposition under reduced pressure is an attractive approach for the conversion of biomass into chemical and fuel products. This approach is characterized by low pressure and short residence time of the vapor products in the reactor. When compared with conventional, atmospheric pressure carbonization, vacuum pyrolysis has the potential to significantly enhance the yields of organic liquid products with respect to solid and gaseous products. The pyrolytic oils obtained from this process can be deoxygenated into transportation fuels (8) and sugars (9) upon further upgrading. Specialty as well as rare chemicals can also be extracted from the oil product (10).

This paper discusses the preliminary engineering data leading to the construction of a vacuum pyrolysis pilot plant for the conversion of wood into oils, chemicals and charcoal.

EXPERIMENTAL

A schematic of the Process Development Unit (P.D.U.) used in this study is shown on Figure 1. The reactor is a multiple-hearth furnace 2 m high and 0.7 m diameter, with six hearths. Heat transfer is provided through heating elements.

At the onset of an experiment wood chips are poured batchwise in a hopper that sits on top of the reactor. The hopper is equipped with a feeding device and is hermetically sealed. For the experiments reported, 6 to 16 kg of wood chips with a granulometry 1/4" to 1/2" Tyler Sieves were fed at a constant rate of 0.8 to 4 kg h⁻¹.

A mechanical vacuum pump removed the organic vapor and gas products from the reactor through a series of outlet manifolds set along the reactor cylinder. Each outlet was connected to a heat exchanger where the vapors were condensed and recovered as liquid into individual glass receivers. Cold tap water circulating on the shell side of the exchangers was used as cooling medium. The vapors from the heat exchange units were collected in a train of receivers that served as a secondary condensing unit. The first receiver was immersed in a bath of a water-ethylene glycol mixture. Receivers 2 and 3 were immersed in baths of dry ice-acetone. Receiver 4 was filled with glass wool at room temperature.

Pressure in the system was lower than 80 mm Hg (absolute) under steady-state conditions. The noncondensable gas was continuously pumped into a 500 L vessel that was set under vacuum at the beginning of the run.

The solid residue was directed toward the bottom of the reactor. The residual charcoal was received in a metallic jar installed on a load cell.

At time zero of the run, wood chips were fed in the preheated reactor. The heating plate temperatures increased from top to bottom of the reactor. A typical temperature profile was 200 °C to 450 °C. The radial temperature gradient for any heating plate was lower than 5 °C during any single run.

The P.D.U. was attached to a central microprocessor that permitted simultaneous data acquisition and control of some 75 operating parameters (64 are recorded and 11 are controlled). Air leakage through the system was lower than 1.3×10^{-3} atm L s⁻¹.

The experiments conducted on the P.D.U. were performed with *Populus deltoides*. The 8-year-old fast-growing poplar clone D-38 was planted in Brockville, Ontario. The sample was essentially all sapwood with no bark. It was shipped to our laboratories in the form of chips by Forintek Canada Corp., Ottawa. Its elemental composition was determined to be 48.2% C, 6.4% H, 45.3% O, 0.09% N, and 0.05% S. Its gross heating value was 4660 kcal kg⁻¹ with an average ash content of 0.6%. Moisture of the air-dry feedstock was determined to be 5.9%.

RESULTS AND DISCUSSION

Yields and mass balance

Results for the operation of the multiple-hearth furnace at varying final thermal decomposition temperature and reactor pressure are presented in Table 1 of the paper. Oil, pyrolytic water, charcoal and gas yields are

presented along with the mass balance calculation for each run. Table 1 indicates that the largest amount of oil is obtained at the lowest pressure and the higher temperature conditions. The oil yield in particular drops sharply with even a slight increase in pressure. Table 1 also indicates that a reactor temperature in the range of 425 - 450 °C is optimum to get the maximum yield of oil from wood. Table 2 summarizes the data obtained for the gas phase composition for the different runs.

Separation of water from the organic liquid phase

One objective of the vacuum pyrolysis process is to produce large quantities of liquid fuels and chemicals from wood. However during the process the liquid organic product is mixed with water (moisture and pyrolytic water). Since extraction of chemicals or further processing of pyrolytic oils mixed with water is difficult and expensive, it is highly desirable to separate the bulk of the aqueous phase from the organic liquid phase.

The separation of water and the organics was achieved during this study by using a series of shell and tube heat exchangers with cool to warm water circulating in the shell section. This series of heat exchangers served as a primary condensing stage for the recovery of the liquid organic fraction. Water was primarily recovered in the series of traps that followed (see Figure 1). The relative proportion of water and oil in both condensing sections is shown in Table 3 of the paper. Table 3 indicates that the lower the pressure, the better the separation between oil and water (see runs C019 and C025). On the other hand at similar operating pressure, the lower the cooling temperature, the more efficient the recovery of oil in the primary condensing section (see runs C023 and C025).

Oil refining

Further fractionation of the wood oil product is necessary if the objective is to either recover pure chemical compounds, or upgrade or process specific chemical group components. Results which are reported by Renaud *et al* (8) and Pakdel *et al* (10) show that the multiple-hearth reactor can be operated in a mode that enables the separation and recovery of selected fractions of liquid fuels and chemicals.

Heat requirement for the pyrolysis reaction

Another engineering parameter to be considered when designing a full scale pyrolysis plant is the amount of energy required for the pyrolysis of each mass unit of wood fed to the reactor. Such value has been empirically determined using the P.D.U. described in this paper, and the detailed procedure has been published elsewhere (11). The determination was based on the difference of electric energy consumed before of after wood was fed to the reactor (heat loss to the atmosphere), and that of the electric energy required for maintaining the multiple-hearth furnace at predetermined set-point temperature with wood chips flowing through the reactor. It was concluded that the heat required for vacuum pyrolysis of aspen wood is about 134 kcal kg⁻¹ of anhydrous wood. Overall, the reaction is slightly endothermic.

Heat required for cooling the organic vapors

The amount of heat removed when cooling the organic vapor products at the primary condensing stage was also experimentally determined (see Figure 1). The heat exchange (Q_w) between the cooling medium (water) and the hot vapor products was calculated using the Equation 1.

$$\text{Equation 1)} \quad Q_w = mC_p (T_{w,in} - T_{w,out})$$

where m is the water flowrate, C_p is the heat capacity for water and $T_{w,in}$ and $T_{w,out}$ is the water temperature at the inlet and the outlet of the heat exchanger, respectively. After taking into account the heat loss to the atmosphere, the overall heat exchanged while cooling the gas and vapor product to 50 °C was found to be 112 kcal kg⁻¹ of air-dry wood.

The experimental set-up simultaneously enabled the calculation of the overall heat-transfer coefficient U for the heat exchangers. The data were plugged in Equation 2.

$$\text{Equation 2)} \quad Q_w = UA (\Delta T)$$

where A is the transfer area and (ΔT) is the temperature driving force. The calculations led to the conclusion that U values vary between 7 and 13 kcal h⁻¹ m⁻² °C⁻¹ according to the position of the heat exchanger attached to the multiple-hearth furnace (11).

Determination of standard heat of reaction

The equipment used enabled us to determine the standard heat of reaction for pyrolysis of air-dry wood chips. For matter of convenience the standard state for wood considered as "a pure substance" was 323 K (50 °C) and 12 mm Hg. The standard heat of reaction was calculated using the Equation 3.

$$\text{Equation 3)} \quad \Delta H^\circ_{323} = \Delta H^\circ_t - \Delta H^\circ_r - \Delta H^\circ_p$$

where ΔH°_r is the total enthalpy change for the reactants from temperature T to 323 K.

ΔH°_p is the total enthalpy change for the products from 323 K to temperature T

ΔH°_t is the enthalpy change for the three-step process including the enthalpy change during the isothermal reaction at 323 K.

Figure 2 illustrates how each term in Equation 3 was empirically determined during run C023. ΔH°_r and ΔH°_p in Equation 3 were calculated using an average heat capacity of 0.5 cal g⁻¹ °C⁻¹ for wood and 0.246 cal g⁻¹ °C⁻¹ for wood charcoal. The value for ΔH°_{323} in Equation 3 was found to be 22 kcal kg⁻¹, which confirms that the reaction is slightly endothermic. Although this value has limiting practical use, it should be viewed as an attempt to improve our theoretical knowledge of thermodynamics of wood pyrolysis.

Calculation of thermal efficiency of the reactor system

The thermal efficiency of the system defined as the ratio of useful energy provided by the vacuum pyrolysis reactor, to the energy supplied to it during a specific period of operations, has been determined for the same experiment C023. The calorific values of the end-products represented the following percentages of the heating value of the initial feedstock: wood

charcoal 36%, wood oil 41% and gas, 5%. Using these data together with values from Figure 2 enabled us to determine that the thermal efficiency was 82%. For this calculation the mechanical pump electric energy requirement was not considered and the reactor was assumed to be perfectly insulated.

Heat transfer phenomena in the reactor

In the pyrolysis reactor, heat can be transferred by conduction, by radiation and by convection. Heat transfer by convection is negligible due to the low pressure conditions in the reactor. Both conduction and radiation play a significant role during pyrolysis and the latter factor is increasingly important at higher temperature levels (12).

The overall heat-transfer coefficient was estimated using the general relation $Q = UA(\Delta T)$. For the multiple-hearth furnace used, the actual heat transfer area used was estimated to be approximately 30% of the total available surface (6 heating plates), since the wood chips moving bed didn't cover the entire section. The transfer area was estimated to be 0.4 m^2 . The temperature driving force was calculated to be 62°C (logarithmic mean), with 25°C and 437°C for the temperature of incoming raw material and the exiting charcoal, respectively, and 200°C and 450°C for the temperature of the top and the bottom heating plate, respectively. With Q_w equal to 150 kcal kg^{-1} (air-dry wood), the overall heat-transfer coefficient was found to be equal to $22 \text{ kcal h}^{-1} \text{ m}^{-2} ^\circ\text{C}^{-1}$.

CONCLUSION

A multiple-hearth reactor has been successfully tested for the production of high yields of liquid fuels and chemicals. The reactor enabled the separation and recovery of water on the one hand and oil fractions or the other hand. Oil yields reached about 50% by weight of the air-dry feedstock.

Heat required for the pyrolysis of wood is slightly endothermic and was determined to be 134 kcal kg^{-1} (on an anhydrous basis). The standard heat of reaction at 323 K and 12 mm Hg was found to be approximately 22 kcal kg^{-1} of air-dry wood. The thermal efficiency of the process is high, in the range of 82%. The overall heat transfer coefficient in the reactor is about $22 \text{ kcal h}^{-1} \text{ m}^{-2} ^\circ\text{C}^{-1}$ which is in range with the existing commercial multiple-hearth furnaces. Preliminary theoretical calculations indicate that a significant reduction of the heat surface area of the reactor can be achieved by operating the reactor at a higher temperature zone in order to enhance the radiative effect.

ACKNOWLEDGMENTS

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FIGURE 1 - SCHEMATIC OF THE VACUUM PYROLYSIS PROCESS DEVELOPMENT UNIT

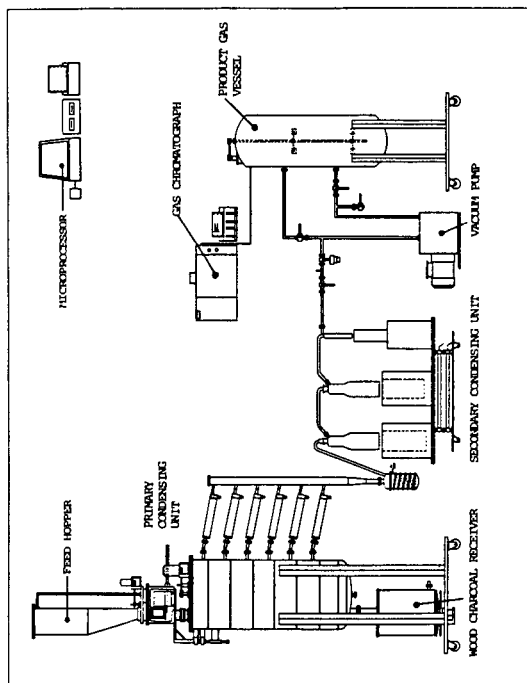


FIGURE 2 - MASS AND ENERGY BALANCES AROUND THE PYROLYSIS REACTOR

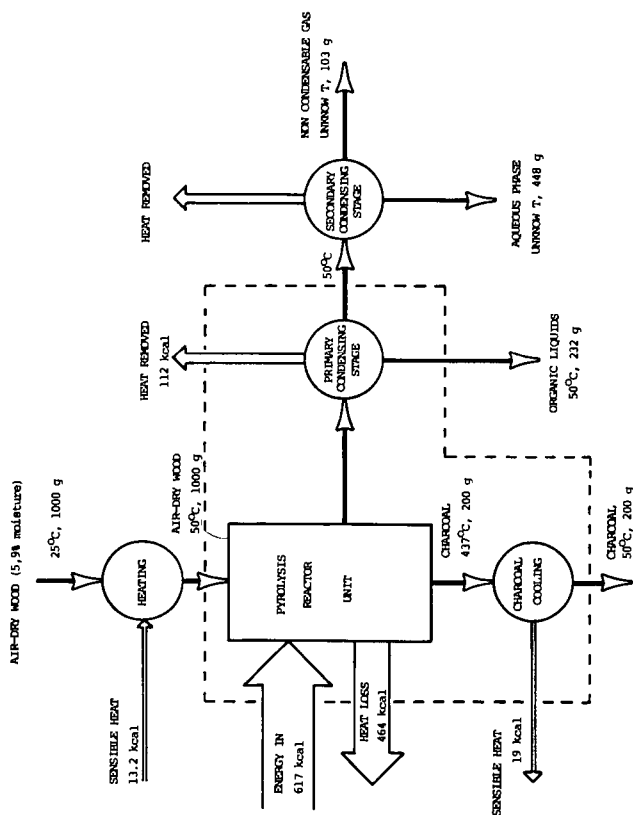


TABLE 1 - YIELDS AND MASS BALANCE FOR VACUUM PYROLYSIS OF WOOD IN A P.D.U.

RUN #	FINAL TEMPERATURE (°C)	REACTOR PRESSURE (mm Hg)	WOOD FEEDSTOCK (kg)	YIELDS (% wt. wood organic basis)				MASS BALANCE CLOSURE
				OIL	WATER	CHARCOAL	GAS	
0010	425	12	5.98	46.4	18.2	24.2	11.2	96.7
0012	363	18	5.99	41.6	14.9	33.0	10.5	97.5
0014	450	25	6.03	45.8	17.0	25.6	11.6	96.1
0015	425	14	6.00	50.1	15.2	25.0	9.7	96.3
0019	465	80	3.39	39.7	21.6	24.7	14.0	96.7
0023	450	12	15.43	50.9	16.5	21.3	11.3	98.3
0024	450	30	18.30	47.4	16.9	25.5	10.2	97.9
0025	450	10	15.99	50.0	15.6	23.0	11.4	98.6

TABLE 2 - GAS PHASE COMPOSITION DURING VACUUM PYROLYSIS OF WOOD IN A P.D.U.

RUN #	FINAL TEMPERATURE (°C)	REACTOR PRESSURE (mm Hg)	TOTAL GAS YIELD (% wt. wood organic basis)	GAS COMPOSITION (% wt.)					OTHERS*	CO/CO ₂
				CO ₂	CO	CH ₄	H ₂	C ₂ -C ₆ HYDROCARBONS		
0010	425	12	11.2	59.2	33.6	2.4	0.9	1.5	2.4	0.57
0012	363	18	10.5	60.4	34.9	0.9	0.1	0.9	2.8	0.57
0014	450	25	11.6	65.7	28.1	1.4	1.0	1.6	2.2	0.43
0015	425	14	9.7	63.8	30.5	1.5	0.8	1.3	2.1	0.48
0019	465	80	14.0	60.0	31.4	3.3	0.7	2.8	1.8	0.52
0023	450	12	11.3	60.7	31.6	2.7	0.0	1.4	3.6	0.52
0024	450	30	10.2	63.5	29.8	2.6	0.7	1.5	1.9	0.47
0025	450	10	11.4	64.6	30.3	1.9	0.4	1.0	1.8	0.47

* Others gases were among the followings = methanol, ethanol, acetone and acetaldehyde.

TABLE 3 - SEPARATION OF WATER AND PYROLYTIC OIL DURING CONDENSATION

RUN #	REACTOR PRESSURE	FINAL TEMPERATURE	COOLING TEMPERATURE	PRIMARY CONDENSING UNIT		SECONDARY CONDENSING UNIT		TOTAL LIQUIDS
	(mm Hg)	(°C)	(°C)	OIL (%)	WATER (%)	OIL (%)	WATER (%)	
0019	80	465	11-28	52.2	19.2	7.4	21.2	2.06
0023	12	450	50-55	32.2	1.5	36.7	29.6	10.45
0024	30	450	30-35	39.8	1.6	27.2	31.4	11.85
0025	10	450	15-20	47.8	3.4	27.2	21.4	10.53

Production of Primary Pyrolysis Oils in a Vortex Reactor

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ABSTRACT

A vortex tube has certain advantages as a chemical reactor, especially if the reactions are endothermic, the reaction pathways are temperature dependent, and the products are temperature sensitive. With low temperature differences, the vortex reactor can transmit enormous heat fluxes to a process stream containing entrained solids. This reactor has nearly plug flow and is ideally suited for the production of pyrolysis oils from biomass at low pressures and residence times to produce about 10 wt % char, 13% water, 7% gas, and 70% oxygenated primary oil vapors based on mass balances. This product distribution was verified by carbon, hydrogen, and oxygen elemental balances. The oil production appears to form by fragmenting all of the major constituents of the biomass.

INTRODUCTION

The pyrolysis of biomass follows a complex set of different chemical pathways, which have thus far not been well established. However, several global pathways have been established, which explain most of the observed phenomena. As shown in Figure 1, the first reaction in fast pyrolysis of biomass is the depolymerization of the lignocellulose macropolymers to form viscous primary oil precursors. These precursors are formed with almost no by-products, and consequently their elemental composition is very similar to the original biomass. With low heating rates, much of the primary oil precursors can repolymerize to thermally stable polymers through the elimination of mostly water to eventually form the material known as char. Physical evidence for a liquid or plastic phase intermediate in the formation of char is the physical shrinkage of the macrodimensions of wood, which takes place during charring (1) in a manner analogous to heat shrinkable polyethylene tubing. If the heating of the biomass proceeds very quickly to temperatures above 450°C, most of the primary oil precursors can crack and vaporize before they form char. In the vapor state, the primary oil molecules are quite dilute, which slows possible second-order polymerization reactions. This dilution allows any unstable primary oil vapors to be converted by first-order reactions to more stable compounds, which can be collected from a reactor designed to have a short gaseous residence time followed by rapid quenching. Thermal stability is relative, however, and these stabilized primary oil vapors readily crack to gases following a global first-order reaction (2). The cracking of the primary oil vapors proceeds with a 10% loss in 36 ms at 700°C and extrapolated 10% losses in 6 ms at 900°C and 591 ms at 500°C.

Obviously, the lower the temperature of the primary vapors in the reactor, the greater the yield of primary vapors which can survive passing through the reactor to the quench zone. Minimizing the time required to travel from the vapor formation zone in the reactor to a lower temperature quench zone also helps to maximize the primary oil vapor yields. The ideal reactor would thus provide large heat fluxes preferentially to the pyrolyzing biomass particle, while not overheating the surface of the particle to cause cracking of the primary vapors to gases as the vapors escape the surface of the particle. The ideal reactor would allow the vapors to be immediately swept away by a colder carrier gas stream out of the reactor to a cold quench zone in order to preserve as much of the vapors as possible. The residence

time of the biomass particles in the ideal reactor must be long enough to ensure complete pyrolysis, but the accumulation of dead char in the reactor is undesirable. It would also be advantageous if the reactor could selectively remove dead char and recycle partially pyrolyzed particles.

The use of thermal radiation for fast pyrolysis has been explored, as this approach preferentially heats the solid with potentially high heat fluxes. However, heating the particle with a high temperature heat source can drive the surface temperature of the particle too high and some vapor cracking would be expected. The use of hot flue gases or hot solids as a heat transfer medium requires that they be at very high temperatures to lessen the amount of the medium which must be generated or recycled; flue gases or hot sand at 900° to 1000°C have been used for fast pyrolysis, but tend to produce higher yields of noncondensable gases from cracking the primary pyrolysis oil vapors to gases as described above. The ideal reactor for the pyrolysis of biomass to primary oils would achieve high heat transfer rates through the use of a mechanism which has an inherently high heat-transfer coefficient, rather than through the use of a high-temperature source. Such a heat transfer mechanism is attained by the conduction of heat from a moderately hot reactor wall directly to the biomass particle.

It can be readily demonstrated that when a stainless steel wire at 500° to 900°C is contacted with a monolithic piece of biomass, the biomass surface is ablatively pyrolyzed and converted to a liquid which allows passage of the wire and to vapors which condense to form smoke. If the stored energy in the wire is transferred to the biomass by sliding the wire across the biomass, pyrolysis rates over 3 cm/sec are observed (3). This method of heat transfer has been studied by pushing a wooden rod into a heated, stainless steel disk, and the pyrolysis rate has been found to be proportional to the pressure exerted and to the temperature difference, where the biomass surface was calculated to be pyrolyzing at 466°C. Heat transfer coefficients as high as 8 W/cm² were reported, which is over 300 times higher than for thermal radiation from a wall at 900°C having an emissivity of one (4).

Although a reactor can be designed to push wooden rods into a hot surface for research purposes (4, 5), most practical biomass feedstocks are expected to be in the form of sawdust or chips. A modified entrained-bed reactor was selected in which the entrained particles enter the reactor tangentially so that centrifugal forces push the feedstock particles onto the externally heated cylindrical wall. Drag forces induced on the particle by the entraining gas stream serve to keep the particles moving on the wall. Since the particles are on or very nearly on the wall, they tend to intercept preferentially the heat, which is conducted through the reactor wall. With nonreacting solid particles in a heat exchanger made from a cyclone separator, the total heat transferred to the process stream was relatively independent of the solids' content at carrier-to-solids (C/S) mass ratios as low as one, whereas with more solids, the heat transferred increased dramatically. The temperature rise in the gas stream was as little as half of that seen in the solids at these low C/S ratios. The heat transfer coefficient from the wall to a solids-free gas was found to follow traditional convective heat transfer relationships, but to be 1.8 times higher in the cyclone than in a straight tube for the same entering tube diameter and entering gas velocities (6). A reported property of a cyclone is that above an entering Reynold's number of 3000, the cyclone has plug flow (7). The cyclone is an interesting reactor concept for the pyrolysis of biomass, as reported in the literature (7, 8). However, the reactor of interest in this paper is a vortex tube, which has many similarities to a cyclone separator.

Vortex tubes have a tangential entrance into one end of a cylindrical tube and an exit at the other end of the tube. If a second exit is added near the tangential

entrance, but in an axial location, a Ranque-Hilsch tube is created which can be fed warm gas in the tangential entrance and produce cold gas coming out of the near axial exit and hot gas out of the far exit. The vortex tube is commercially used for reliable refrigeration where the cost of the compressed gas is of no concern. Research into the aerodynamics of the vortex tube revealed that in the Ranque-Hilsch tube there was an outer vortex which exited the hot end and an inner vortex which exited the cold end. If the cold end was not open, the vortex tube was reported to have a third concentric vortex, which flowed toward the hot end (9). The pitch of the vortex near the cylindrical wall was reported to be about 1.2 times the diameter of the vortex tube. This results in a coarse helical path of the gases near the wall, as measured by pitot tubes (9, 10). This coarse helical path on the wall also exists for the more conventional cyclone separator (11). The effect of the coarse path is that entrained solids, which are centrifuged to the wall, follow the same coarse path through the reactor. This has two deleterious effects: only a narrow path of the cylindrical wall would be used for heat transfer; and the residence time of the solid particles is only a fraction of what it would be with a tighter helical path.

The vortex tube reactor which we developed is shown in Figure 2 and has some unique features, which were found necessary to achieve the desired reactor performance in the fast pyrolysis of biomass. The carrier gas is pressurized to between 75 and 150 psia, depending upon the desired flow rate, and passes through a supersonic nozzle. Biomass in the form of minus 3-mm sawdust is metered into, and is entrained by, the supersonic carrier gas stream. Cold-flow studies with 4000-frames-per-second movie coverage established that this entrainment method results in rapid acceleration of the sawdust particles to velocities over 125 m/s. The cold-flow studies also verified that the entrained particles were following the reported coarse path of the gas flow near the wall. This coarse helical path appeared to be independent of the entrance angle, the entrance duct shape, and the flow rate of the carrier gas (12). The pitch angle of the solids flow in the conical section of a conventional cyclone was observed to be about one-fifth that in the cylindrical section (11), but the cylindrical vortex tube has more heat-transfer surface area per unit length. To force the entrained particles into a tight helical path, the 316 SS cylindrical vortex tube wall was machined to leave a 3-mm high and 3-mm wide raised helical rib. High-speed movies taken of the cold-flow system verified that the raised rib forced the solids to take the desired tight helical path (13). A tracer gas experiment, following the progress of propane pyrolysis, verified that this reactor design was essentially plug flow, with the inner vortices contributing a very small amount of internal recycling (14).

Initial operation with this vortex tube as a reactor for the fast pyrolysis of biomass was with heating the reactor wall to relatively high temperatures of 800°C or so. At that time, the goal was to crack the primary vapors to gases, rather than the preservation of the primary oils. Under these conditions, the sawdust had ample time to pyrolyze, as well as the char having time to partially gasify to produce char yields of only about 5%. However, as the vortex reactor wall became hotter, the tendency increased to accumulate a layer of secondary tar and char on the wall. By reducing the wall temperature to 625°C, the buildup of an insulating char-tar layer became negligible, but the rate of pyrolysis of the sawdust particles was so low that about 30% of the feed could be recovered in the char cyclone as scorched feed. A tangential exit was then added to the vortex tube reactor to allow the unreacted feed and large char particles to be recycled to the entrance of the reactor. The carrier gas nozzle acts as an ejector to create the pressure differential to drive the recycle loop. The recycle stream blows the sawdust off the feeder screws to positively entrain the feed to the carrier gas ejector.

The temperature at the exit of the insulated, but unheated, recycle loop is typically 400° to 450°C. The carrier gas is preheated to between 600° and 700°C prior to expansion through the ejector nozzle. With these conditions, the temperature of the pyrolysis stream is 480° to 520°C, as it exits the vortex reactor system. About 10% of the feed is converted to char, which is recycled with the scorched feed until it is attrited to less than 50 micrometers in size. The vortex reactor system acts as a particle size classifier, and the char fines are entrained out of the vortex system to be removed by a cyclone separator having a higher collection efficiency. The fine char has a volatile content of 15% to 20% and burns readily, especially when hot. The bulk density of the fine char is between 0.18 and 0.24 g/mL, depending upon whether it was freshly poured or has been allowed to settle (the bulk density of the sawdust feedstock was 0.24 g/mL). The empirical formula for this volatile char is $\text{CH}_{0.53}\text{O}_{0.12}$, and it has a heating value (HHV) of 33 kJ/g (14,000 Btu/lb). A microscopic examination of the char fines shows that the particles have the appearance of broken thin-walled tubes; i.e., charred and broken cell walls.

As noted above, the primary vapors are cracking significantly even at 500°C and a residence time of half a second. If the recycle loop of the vortex reactor is removed, the yield of permanent gases is about 3%, based on the reacted feed. The initial gases, which are formed under these conditions, are extraordinarily rich in carbon dioxide and are associated with the formation of char. With the recycle loop open, some of the primary pyrolysis vapors are recycled along with the carrier gas, unreacted solids, and large char. The additional time, which the recycled primary vapors spend in the vortex reactor leads to a small loss in the yield of primary vapors and a higher yield of noncondensable gases of about 7%. The composition of the gases shifts considerably from the initial gases formed to that associated with a small loss of primary vapors. An even greater shift in the gas composition occurs with more extensive cracking of the primary vapors to produce an asymptotic gas composition as the primary vapors near extinction, which is low in carbon dioxide, as shown in Table 1.

The experimental determination of the feed consumed, the char yield, and the noncondensable gas yields are relatively straightforward. However, the primary vapor and water yields have proven difficult to measure directly due to the formation of aerosols. These aerosols escape high-pressure sprays, cyclonic separators, and impingement or inertial collection techniques. The use of condensable steam as the carrier gas makes the water yield very sensitive to small measurement errors in the steam carrier gas flow. The use of noncondensable gases as the carrier tends to strip the volatile organics and the water of pyrolysis from the condensate. These considerations have led to the use of a noncondensable carrier gas, nitrogen, and to the determination of the water formed during pyrolysis and the primary oil yield by difference. By analyzing the recovered condensate for water, the yield of water may be determined. These techniques led to the conclusion that yields of about 70% primary vapors were achieved, based on taking the difference between the sawdust fed and the measured gas flow and char collected, correcting for the water content of the condensates. After elemental compositions were obtained for the feed and the collected products, an elemental balance was computed which verified the high primary vapor yields of 69 to 77 wt %, as shown in Table 2, based on the yield of recovered char (2).

The primary pyrolysis oils, which have been recovered from the vortex reactor, are highly oxygenated and have nearly the same elemental composition as the biomass feedstock. The oils have a dark brown color and are acidic with a pH between two and three. The heating value (HHV) of the dry oils is 20 to 22 kJ/g (8700 to 9500 Btu/lb). The oils can absorb up to about 25% water before forming two

phases. The viscosity of the oils was 1300 cp at 30°C, and the density was 1.3 g/mL (15). Although the primary vapors have a low molecular weight as determined by the FJMBMS (16), they rapidly polymerize upon physical condensation to form high-molecular-weight compounds in the oils (17). Attempts to slowly distill the oils led to the rapid polymerization of the oils boiling above 100°C (15). The oils have significant chemical activity, which suggests their potential use in low-cost adhesives, coatings, and plastics.

The concept of supplying heat through the wall of a vortex reactor to drive endothermic processes is in its early development. The scale-up potential of this concept depends upon the angular momentum of the swirling carrier gases to keep the entrained feed particles moving on the wall. The heat flux delivered to tubular pyrolysis reactors typically ranges between 5 and 15 W/cm² (20,000 to 50,000 Btu/hr-ft²). Reported data for vortex tubes indicates that with diameters larger than 2.5 cm most of the angular momentum is retained even after traveling a tube length equivalent to 20 tube diameters. The major momentum losses are due to the frictional contact of the solids and the gases with the vortex-tube wall. With larger vortex tubes needed for scale-up, the angular momentum of the process stream will increase more than the frictional losses. The heat transferred to the reactor will scale by the product of the diameter AND the length. These considerations have led to calculations which suggest that a vortex reactor with a 250 TPD capacity would have a diameter of only about 0.5 m and a length of 9 to 12 m. The fabrication technique would most likely be by the welding up of a spirally wrapped tube to form the raised, helical rib.

CONCLUSIONS

For the fast pyrolysis of biomass, a vortex reactor has significant advantages for the production of primary pyrolysis vapors, including: high heat transfer coefficients which allow the use of moderately low temperatures of the vortex reactor walls to supply the endothermic heat of pyrolysis; separation of the partially pyrolyzed feed particles from the char; the ability to recycle the partially pyrolyzed feed; the ability to accept a wide spectrum of particle sizes in the feed; short gaseous residence times; nearly plug flow; and preferential heating of the solid feed over the vapor stream, to preserve the primary vapors. Primary pyrolysis vapor yields in the 70% range have been calculated by mass balances and verified by elemental balances, although physical collection of these vapors has proven to be elusive due to the formation of persistent aerosols and due to the volatility of the vapors in the carrier gas (methods to recover these vapors more completely with practical means are under development).

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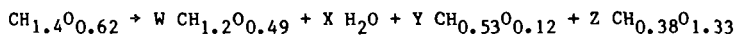
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Table 1. Pyrolysis Gas Composition at Various Cracking Severities (mol %)

	Vortex Exit Gases w/o Recycle (Run 34)	Vortex Exit Gases w/Recycle (Run 58)	Severely Cracked Vapor Gases (Run 58)
H ₂	3.4	8.3	17.8
CO	46.2	49.2	52.2
CO ₂	43.1	27.6	7.5
CH ₄	4.6	8.9	12.0
C ₂ H ₂	--	0.1	1.1
C ₂ H ₄	1.3	2.4	5.9
C ₂ H ₆	0.3	0.7	0.6
C ₃ H ₈	0.1	0.1	--
C ₃ H ₆	0.4	0.8	0.8
C ₄ H ₈	0.3	0.3	0.6
C ₅ +	0.5	1.4	1.4
wt % yield of gases	~4	~6	65%

Table 2. Elemental Balance for Fast Pyrolysis to Primary Vapors

Feed + Primary Vapors + Water + Char + Gas



Exp. Char Yield	Calculated Product Values, Wt %		
	Primary Vapors	Water	Prompt Gas
7.5	76.8	11.7	4.0
10.5	73.1	12.8	4.1
12.7	69.0	14.0	4.3

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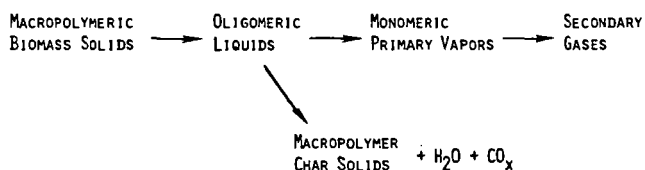


FIGURE 1. GLOBAL REACTIONS IN FAST PYROLYSIS

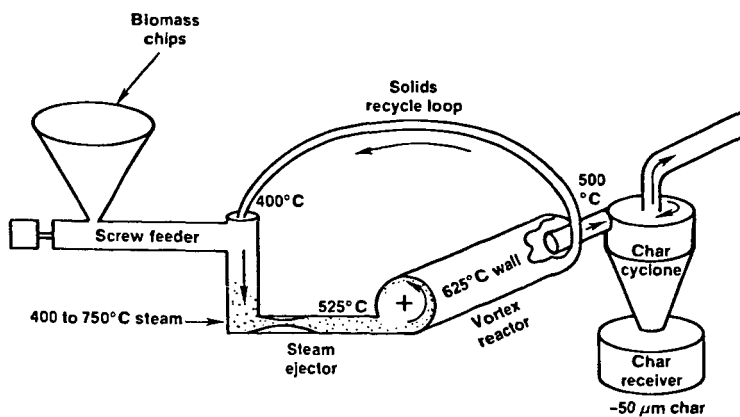


FIGURE 2. VORTEX REACTOR SCHEMATIC

FAST PYROLYSIS OF PRE-TREATED WOOD AND CELLULOSE

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Introduction

Over the last several years, the Waterloo Fast Pyrolysis Process (WFPP) has been developed to maximize yields of liquids by the rapid thermal decomposition of lignocellulosic biomass. The process operates at atmospheric pressure and the reaction is carried out in a fluidized bed of sand as a heat transfer medium. Optimal conditions for woody biomass are 450°-550°C and about 0.5 seconds gas residence time. The nature of the fluidizing gas has little influence on yields.

Liquid yields from wood at optimal conditions are 70%-80% of the dry feed, with the organic liquid yields being 60%-65% of the dry wood fed. A description of the process and the yields obtained with various types of biomass has been published previously by the authors (1)(2). Extensive identification and quantification of many of the individual compounds present in these pyrolytic oils have also been reported (3)(4)(5).

Shortly before his death, Shafizadeh suggested (6) that pre-treatment of the wood by a mild acid hydrolysis to remove hemicelluloses followed by pyrolysis of the wood would allow a higher yield of fermentable sugars to be obtained, because the pentoses could be recovered from the acid hydrolysate and added to the anhydrosugars customarily formed in wood pyrolysis oils. However, this argument overlooked the fact that very low yields of anhydrosugars are normally obtained from wood except under slow heating at low temperatures (and perhaps vacuum) conditions. Certainly, yields of anhydrosugars and glucose from the rapid pyrolysis of wood in the WFPP are usually less than 5%. However, it was decided in this work, for other reasons, to investigate the effect on pyrolysis yields, and on the composition of the liquid product, of a mild pre-hydrolysis to remove part or most of the pentoses while leaving the cellulose content unaffected. The results of preliminary work are reported here.

Experimental

Samples of a standard poplar wood and of commercial cellulose products (IEA hybrid poplar, SS-144 chromatographic celluloses and Avicel pH 102 microcrystalline cellulose) were used as test materials. Properties of these feeds are given in Table 1.

Pyrolysis of raw and treated wood or cellulose was carried out at standardized conditions for all runs (500°C, 0.46 seconds gas residence time, N₂, -590 µm particle size) using the bench

scale fluidized bed apparatus which has been described elsewhere (1). Methods of analysis of tar, gas, char and water yields has also been described previously (2).

Wood or cellulose was hydrolyzed in a batch reactor at 90°C using sulfuric acid concentrations of 1%, 3% and 5% with reaction times of 6 or 19 hours and liquid to solid weight ratios of 4:1 or 12:1. A summary of reaction conditions is given in Table 1. Hydrolysis conditions were selected to give a high degree of conversion of the glucuronoxylan, which is the principal component of hardwood hemicellulose, to xylose, while leaving the cellulose unaffected. After treatment, the sample was filtered, washed to a pH of 6.3 and dried at room temperature.

Analysis of acid hydrolysate and of the water extract of the pyrolysis oils was done by HPLC (Aminex HPX-87H column at 65°C, eluent 0.07 N H_3PO_4 , eluent flow rate 0.32 x 2.25 ml/min).

Results

Table 2 shows the amount of xylan removed during the various acid treatments. The calculated percent removal is based on an assumed value of 20.5% by weight of pentosans in the IEA poplar (7). The total weight loss from the wood exceeded the equivalent amount of xylose recovered, because of the hydrolysis of some lignin and some minor hemicellulose constituents. The results of Table 2 suggest that at even the mildest hydrolysis conditions (1% H_2SO_4 at 90°C for 19 hours at a 4:1 liquid to solid ratio) most of the readily hydrolyzable xylan has been converted to xylose. Changing the liquid to solid ratio at constant acid strength had little effect, indicating the relative completeness of the initial hydrolysis reactions of hemicellulose. Also shown in Table 2 are the blank run carried out using hot water only, as well as the conditions for the acid treatment of the commercial celluloses used.

The results of the pyrolysis runs for the untreated and treated poplar wood are given in Table 3. The two runs in which most of the xylan was removed by acid hydrolysis gave a 78%-80% yield of organic liquid, and a greatly reduced yield of water. The char and gas yields were also reduced to about one half the value of that for the untreated wood. Table 4 gives the analyses of the organic liquid fraction produced in the pyrolysis runs shown in Table 3. The most notable feature is the sharp increase in levoglucosan and in total sugar content of the oils from the acid hydrolyzed wood, while a sharply reduced yield of hydroxyacetaldehyde occurred simultaneously. A marked decrease in the amounts of acid produced from treated wood is also apparent.

Similar results are shown in Table 5 for a commercial low ash cellulose (SS144) which gave high yields of hydroxyacetaldehyde from pyrolysis at 500°C, and much less levoglucosan. After a mild hydrolysis, levoglucosan yield was sharply increased, and that of hydroxyacetaldehyde decreased. A large increase in

cellobiosan yield was also observed for both this cellulose and for the treated wood.

Results for the pyrolysis of untreated and for acid washed Avicel PH-102 are also given in Table 5. Again, a large increase in levoglucosan yield and an almost zero yield of hydroxyacetaldehyde result from acid washing. The yields of acids and of other minor constituents is also sharply decreased for the acid washed Avicel, although cellobiosan yield increases.

The hydrolysate liquors from wood were analyzed for Ca, Mg, Na and K contents, which were compared to those found from analysis of the ash from the untreated wood. Essentially all these cations were removed in the acid treating step.

Discussion

The reason for the great increase in levoglucosan and the parallel decrease in hydroxyacetaldehyde yield following acid treatment is not clear from these results. It is tempting to say that the change in product distribution is due to the removal of inorganic cations during the acid treating process, since it is known that these cations can catalyze the decomposition of cellulose and its degradation products. However, the low ash content SS144 cellulose also showed this remarkable increase in levoglucosan yield. Also a comparison of results for the untreated and the acid washed Avicel PH102 microcrystalline cellulose (average ash content 40 ppm) also shows an increase in levoglucosan yield from 27.0%-38.4% of the feed when pyrolyzed at 500°C while hydroxyacetaldehyde and cellobiosan decreased from 8.6%-0.43% and 10.1%-5.6% respectively.

While there is little doubt that the content of inorganic cations affects the product distribution, it appears that it is not the only effect, and the morphology and degree of hydrogen bonding in the cellulose must also influence the composition of the pyrolytic liquids.

Apparently, the xylan content of wood is a primary source of much of the gas and char formed in fast pyrolysis, as well as being a major contributor to the acid content of the pyrolytic oils.

When the results of Tables 3 and 4 are recalculated on the basis of cellulose content, then it is found that fast pyrolysis of the acid treated wood can convert 75% of the cellulose to sugars - largely anhydrosugars, with 15% reducing sugars and 15% disaccharides. When the pentose content of the acid hydrolysate is added to this, a high conversion of the wood to sugars is obtained, with about 80% of the holocellulose content yielding sugars of various kinds. Fast pyrolysis of acid treated wood may well be an economical route for the production of fermentable sugars, as Professor Shafizadeh suggested.

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Table 1
Properties of Feed Materials

Source	Cellulose		Poplar Wood
	Avicel pH 102	Schleicher & Schuell #144 TLC Cellulose Powder	Clean Wood Only Ontario MNR Clone D-38
Moisture, wt%	2.9	4.0	4.6
Ash, % mf	< 0.01%	0.062	0.46
Elemental Analysis, %			
C	44.3	44.4	49.45
H	6.16	6.17	6.05
O	49.5	49.4	44.4
N	Tr	Tr	0.07
Cellulose (Typical) %	> 99	> 95	42.3
Hemi Cellulose (Typical) %	--	--	31.0
Lignin (Typical) %	--	--	16-22

Table 2
Hydrolysis Conditions for Wood and Cellulose

Run No.	Residue After Hydrolysis grams*	Acid Conc.	Time hrs.	Temp °C	Liquid: Solid	Xylose Conc.	% of Xylan Removed
A-1 (Wood)	106	5%	6	90	4:1	3.24%	67%
A-3 (Wood)	101.2	1%	19	90	4:1	2.5%	51%
A-4 (Wood)	=150	None	5.5	90	4:1	Tr	Tr
A-5 (SS-144)	=150	5%	5.5	90	4:1	Tr	--
A-6 (Avicel)	=150	5%	5.5	90	4:1	N11	--

* Initial amount in all tests was 150 grams

Table 3
Pyrolysis of Raw and Treated Wood
Overall Product Yields

	PP 59	A-2	A-4	A-3	A-1
Feed	Poplar Wood Pilot Plant	Poplar Wood Bench Unit	Wood Hot H ₂ O ext.	Wood Very Mild Hyd.	Wood Mild Hyd.
Feed Rate, gm/hr	3,390	29.6	33.4	16.2	21.9
Temp °C	504	497	504	503	501
Vapor Res. Time, s	0.48	0.46	0.46	0.46	0.45
Particle Size, μ m	-1000	-590	-590	-590	-590
Moisture, %	4.6	3.3	7.0	0.83	16.5
Cellulose, %	49.1	49.1	50.0	63.4	62.8
Yields, % Wood mf					
Organic Liquid	66.2	65.8	69.8	78.3	79.6
Water	10.8	12.2	7.6	5.0	0.9
Char	11.8	7.7	9.3	6.0	6.7
Gas	11.0	10.8	12.3	7.7	6.4
	<u>99.8</u>	<u>96.5</u>	<u>99.3</u>	<u>97.0</u>	<u>93.6</u>

Table 4
Pyrolysis of Raw and Treated Wood
Analysis of Organic Liquids

	PP 59	A-2	A-4	A-3	A-1
Yields of Tar Components % mf Feed					
Oligosaccharides		0.7	2.58	3.80	1.19
Cellobiosan		1.3	3.18	10.08	5.68
Glucose		0.4	1.0	1.67	1.89
Fructose		1.31	2.35	4.00	3.89
Glyoxal		2.18	3.68	4.10	0.11
1,6 Anh. Glucofuranose		2.43	4.12	3.08	4.50
Levoglucoosan	<1	3.04	5.17	15.7	30.42
Hydroxyacetaldehyde	8.86	10.03	12.61	5.35	0.37
Formic Acid		3.09	3.42	2.54	1.42
Acetic Acid	4.33	5.43	5.20	1.46	0.17
Ethylene Glycol		1.05	0.78	0.43	-
Acetol	2.93	1.40	1.20	0.06	0.06
Methylglyoxal		0.65	1.28	0.41	0.38
Formaldehyde		1.16	1.78	0.72	0.8
Aromatics (lignin)	\downarrow by G.C.	16.2	-	18.0	19.0
Totals		51.5	-	71.4	69.9
% of Pyrolysis Oil		78.3	-	91.2	87.8
Sugars		9.2	18.4	38.3	47.6

Table 5
Pyrolytic Products from Celluloses

Run Source	SS-12 Commercial SS 144	A-5 Treated SS 144	6 Avicel pH-102	A-6 Treated Avicel
Temp °C	500	502	500	503
Yields, % mf of feed				
Organic liquid	72.5	83.5	87.1	86.3
Water	10.8	6.1	3.1	?
Char	5.4	1.3	2.5	5.7
Gas	7.8	3.9	8.9	3.3
Hydroxyacetaldehyde	15.3	6.2	8.6	0.43
Levogluconan	7.0	31.8	26.9	38.41
Cellobiosan	4.0	11.5	10.1	5.6
Glucose	1.0	1.8	2.1	2.0
Fructose	2.0	3.0	4.7	2.7
Glyoxal	3.5	5.5	6.5	2.1
Methylglyoxal	0.8	1.3	0.23	0.30
Formic Acid	5.5	1.9	3.8	1.5
Acetic Acid	4.9	0.1	1.4	0.03
Ethylene glycol	1.7	0.02	0.56	0.00
Formaldehyde	1.2	0.94	0.72	0.24
Acetol	2.2	0.12	0.04	0.02
Anhydroglucofuranose		5.5		7.0
Oligosaccharides		5.3		
% of Oil Quantified		89.6		